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BRANDEIS UNIV WALTHAM MASS DEPT OF CHEMISTRY
CRYSTAL AND MOLECULAR STRUCTURE OF $(\text{Ni}((\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3)_2) \text{ (---ETC(U))}$
FEB 78 B M FOXMAN, H MAZUREK
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Contract No. N00014-76-C-0822

Task No. NR 053-619

TECHNICAL REPORT No. 2

Crystal and Molecular Structure of $\{ \text{Ni} [(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3]_2 \}$
 $\{ \text{Ni} [\text{NCS}]_4 [\text{P} (\text{CH}_2\text{CH}_2\text{CN})_3]_2 \}$: A β -Hydroxyketone Chelate Complex

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Prepared for Publication

in

Inorganic Chemistry

February, 1978



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AD A 053718

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER Technical Report No. 2		2. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Crystal and Molecular Structure of {Ni- [(CH ₃) ₂ C(OH)CH ₂ COCH ₃]}{Ni[NCS]}[P(CH ₂ - CH ₂ CN)] ₂ : A β-Hydroxyketone Chelate Complex		5. TYPE OF REPORT & PERIOD COVERED Interim Repts.	
10. AUTHOR(s) Bruce M. Foxman Harry Mazurek		15. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0822	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Brandeis Univ. Waltham, MA 02154		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-619	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE Feb 78	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 27	
		15. SECURITY CLASS. (of this Report) Unclassified	
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES Submitted to Inorganic Chemistry			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Nickel Halophosphines, β-hydroxyketone chelate, isothiocyanate complex			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See page 1			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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Crystal and Molecular Structure of $\{ \text{Ni} [(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3]_2 \}$
 $\{ \text{Ni} [\text{NCS}]_4 [\text{P} (\text{CH}_2\text{CH}_2\text{CN})_3]_2 \}$: A β -Hydroxyketone Chelate Complex

by Bruce M. Foxman* and Harry Mazurek

Contribution from the Department of Chemistry

Brandeis University, Waltham, MA 02154

ABSTRACT

The title compound has been synthesized and its crystal structure determined by single-crystal X-ray diffraction methods. The complex crystallizes in space group $\bar{P}1$, with $a = 12.773(4)$, $b = 11.421(3)$, $c = 8.864(3)$ Å; $\alpha = 106.37(5)$, $\beta = 78.56(5)$, $\gamma = 104.37(5)$ degrees. Full-matrix least-squares refinement of positional and thermal parameters for all atoms (3 methyl H atoms fixed), with 3610 reflections ($F > 3.92 \sigma(F)$) led to $R = 0.044$ and $R_w = 0.064$. Both cation and anion occupy crystallographic centers of symmetry. In the cation, the β -hydroxyketone ligand is (as expected) not planar: the hydroxyl oxygen atom and β -carbon atom lie $+0.40$ and -0.38 Å out of a plane containing Ni and the other ligand atoms. The Ni-O distances to the carbonyl and hydroxyl oxygen atoms are $1.895(3)$ and $1.927(3)$ Å, respectively. The anion is trans-octahedral; Ni-N-C angles show large distortions from linearity: $160.7(3)$ and $163.9(3)^\circ$.

Introduction

Square-planar nickel(II) complexes of the polyfunctional phosphine ligand tris-(2-cyanoethylphosphine) (hereafter, CEP) undergo a series of interesting solid-state transformations.^{1,2} We have endeavored to study such solid-state processes, using CEP, various transition metals (Ni, Pd, Pt, Fe, Co), and halide or pseudohalide anions (F^- , Cl^- , Br^- , I^- , SCN^-). In one of several attempts to synthesize various $NiCEP_2(NCS)_2$ phases, the title complex was formed in very poor yield. Since only a very small amount of the material was available, the most feasible method of analysis was deemed to be a single-crystal X-ray structure determination.

There are numerous examples of transition metal-oxygen chelate complexes in the chemical literature, particularly acetylacetonate complexes.³ However, we believe this to be the first reported discovery and X-ray structural characterization of a neutral β -hydroxyketone, 4-hydroxy-4-methyl-2-pentanone, (hereafter diacetonealcohol), acting as a bidentate ligand.

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Experimental

The crystal used in this study was synthesized by a technique similar to that employed for the syntheses of NiX_2CEP_2 complexes ($\text{X}=\text{Cl}, \text{Br}$).¹ Apparently, an aldol condensation occurred during one of the preparations, and a pale yellow-orange material (~ 100 mg) deposited, instead of the usual product, red $\text{Ni}(\text{NCS})_2\text{CEP}_2$. All attempts to reproduce that preparation, the details of which are available from the authors, invariably failed. Further, attempts to prepare the complex directly from diacetonealcohol, $\text{Ni}(\text{NCS})_2$ and CEP led only to $\text{Ni}(\text{NCS})_2\text{CEP}_2$. We have devised a preparation of this elusive material, which is a relatively reproducible preparation of the complex in poor yield:

$[\text{Ni}(\text{diacetonealcohol})_2][\text{Ni}(\text{NCS})_4\text{CEP}_2]$. -- $\text{Ni}(\text{NCS})_2$ (0.50 g, .0029 mol, ROC/RIC), CEP (0.44 g, .0023 mol, Aldrich), 12 ml absolute EtOH, 10 ml reagent grade acetone, 2 ml triethyl orthoformate, 0.5 ml t-BuOH and ~ 10 mg K(t-OBu) are mixed in a 25 ml flask. The flask is kept at -10°C for 17 hours, removed, and the mixture poured onto a filter paper in a Büchner funnel. The funnel and a tight-fitting vial (to collect the liquid) are placed in a warm (~ 30°C) area. After the flocculent precipitate dries to a cake, it is removed, and a small amount of pale yellow-orange crystals are found on the paper! More sophisticated (and intelligent) approaches to the synthesis of this

material were attempted, to no avail. The magnetic susceptibility of the complex at 25°, $\chi_m^{\text{corr}} = 4.23 \times 10^{-3}$ c.g.s.u, leads to $\mu = 3.17$ B.M.

Collection and Reduction of Diffraction Data. -- Preliminary Weissenberg (0kl, lkl) and precession (hk0, hkl, h0l, hll) photographs showed neither systematic absences nor symmetry, leaving space groups P1 or $\bar{P}1$ as possible choices; the latter was confirmed by successful refinement of the structure. A Laue photograph of the crystal indicated it to be of excellent quality, and it was transferred to a Supper No. 455 goniometer and centered optically on a Syntex P2₁ diffractometer. Most operations were carried out as described previously⁴; other operations are described below. Details of the structure analysis, in outline form, are presented in Table I.

Solution and Refinement. -- Initial computational work was carried out on a limited data set using the Brandeis University PDP-10 computer, using local versions of programs described previously.^{4,8} The analysis was completed some time later on a Syntex XTL Structure Determination System (24K Nova 1200 configuration).⁹ The analytical scattering factors of Cromer and Waber were used^{10a}; real and imaginary components of anomalous scattering were included in the calculations for all nonhydrogen atoms.^{10b} The structure was solved with difficulty from a rather

complicated three-dimensional Patterson map. The map has its largest peak at $(\frac{1}{2}, 0, \frac{1}{2})$, and the appearance of peaks (~ 8) about the latter was similar to the distribution about the origin. It was thus apparent that two independent centers of symmetry were occupied by dissimilar ions. The trial structure was deduced from chemical considerations and the experimentally-determined X-ray molecular weight of the unit cell. A trial structure factor calculation using derived coordinates for Ni1, Ni2 and P gave $R = 0.492$. The remaining atomic positional parameters were obtained (with some difficulty due to poor phasing) from successive difference Fourier syntheses. At the conclusion of anisotropic refinement of all nonhydrogen atoms, a difference Fourier synthesis revealed the positions of all hydrogen atoms. These refined successfully except for the methyl hydrogen atoms attached to Cl6. For these the program METHYL¹¹ was used to generate tetrahedral positions for the methyl H atoms at 10° intervals about the Cl5-Cl6 bond axis. Calculated H atom positions were then selected, which were the "best fit" to the set of three observed H atom positions. These three H atoms (H16A,B,C) were included, as fixed contributions to F_c (with C-H = 0.95 Å) in subsequent cycles of least-squares refinement. The calculation procedure above was repeated after each cycle of refinement. At convergence, $[(\Delta/\sigma_{\max}) \leq 0.09]$, a weighting scheme analysis revealed no systematic dependence of $w[|F_o| - |F_c|]^2$ on $|F_o|$, $\sin \theta/\lambda$, parity of indices or sequence

number. Table II lists the positional and isotropic temperature factors for all atoms, while anisotropic temperature factors appear in Table III.

Results and Discussion

$[\text{Ni}(\text{diacetonealcohol})_2]^{2+}$. -- Various features of the molecular structure of the cation, including the location of the ROH hydrogen atom, are depicted in Fig. 1. Examination of pertinent bond distances and angles (Table IVA) confirms the formulation of the cation as a bis(β -hydroxyketone) chelate complex. For this square-planar complex, the shortest intermolecular contact to nickel, Ni2-S2, is 4.09 Å. Features which distinguish this ligand from the closely-related, planar acetylacetonate ligand and its complexes are:

(i) atoms Ni2, O1, C12, C13 and C14 lie in a plane with deviations < 0.03 Å, while atoms C15 and O2 are each ~ 0.4 Å out of the plane (Table V);

(ii) the β -carbon atom, C15, and the hydroxyl oxygen atom O2, are approximately tetrahedral while C12 is essentially trigonal planar (Tables IV and V);

(iii) the Ni2-O2 distance, 1.927(3), is, as expected, significantly longer than the Ni2-O1 distance, 1.895(3). The latter compares well with Ni-O distances of 1.881(5) and 1.896(5) in $\text{Ni}[\text{P}(\text{C}_6\text{H}_{11})_3](\text{CH}_3)(\text{acac})$,^{3c} but is longer than the Ni-O distance

of 1.836(5) in bis(dipivaloylmethanido)nickel;^{3e}

(iv) the C-O distance, 1.268(5) Å, is in the range observed for various acac complexes, e.g. 1.264(5),^{3d} 1.279(5),^{3a} and 1.314(10)^{3e} Å. The C-O_{hydroxyl} distance, 1.498(5) Å, is also within the range of published values for transition-metal alcohol complexes.¹²

(v) the "bite angle" of this ligand is 90.30(13)°, somewhat smaller than that observed for nickel β-diketone complexes, e.g. 94.6(4)^{3e} and 92.9(4)°^{3c}. In the same two examples, Ni-O-C angles lie in the range 126-128°. Here, the Ni-O_{ketonic}-C angle is somewhat larger, 132.14(27)°, while the Ni-O_{hydroxyl}-C angle is considerably smaller, 117.45(24)°. An indication of strain in this ring system is also given by the Cl2-Cl4-Cl5 angle of 118.10(35)°.

[Ni(NCS)₄CEP₂]²⁻. -- The molecular structure of the anion, showing 50% probability ellipsoids for atoms refined anisotropically, is depicted in Fig. 2. The phosphine ligand geometry is normal for CEP complexes.^{2,13} The Ni-P (2.420(1)) and Ni-N (2.068(3), 2.072(3)) distances are similar to those found in octahedral, polymeric NiX₂CEP₂ complexes [X=Cl, Ni-P:2.438(1), Ni-N(nitrile):2.099(2); X=Br, Ni-P:2.445(1), Ni-N(nitrile):2.082(3)].^{2,14}

Large deviations from linearity occur in the Ni1-N1-Cl and Ni2-N2-C2 angles, 160.77(26) and 163.90(28)°, respectively. Inspection of Table V shows that these deviations occur largely

in the Ni1-N1-P and Ni1-N1-N2 planes. This apparently occurs with some distortion of the P-Ni1-N1 and Ni1-Ni1-N2 angles from 90° (Table IVB). Apart from weak hydrogen bonding to S2 (vide infra), the reason for these distortions is obscure. There are no unusually short inter- or intramolecular contacts to the thiocyanate groups. It appears (Fig. 2) that the distortions are consistent with a complex conformation of relatively low energy. It has been demonstrated that large variations in bond angles may arise in closely related conformers of transition-metal complexes.¹⁵ In any event, the M-N-C angles are within the range of reported values (140-180°).¹⁶

Crystal Structure. -- The crystal structure (Fig. 3) consists of discrete anions and cations, with a weak hydrogen bond (dotted line in Fig. 3, S2...HO2-O2). The S-O distance is 3.41 Å and the S2-HO2-O2 angle is 166.6°. There are no other short or significant contacts ≤ 3.8 Å. It has been demonstrated that $M(NCS)_n$ compounds, where M is a first-row transition metal and $n = 4$ through 6, are stabilized by large cations of preferably equal but opposite charge.¹⁶ It seems likely here that the anion/cation effect is mutual.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (Table VI) (n pages). Ordering information is given on any current masthead page.

Acknowledgements: We gratefully acknowledge support in part by the Office of Naval Research, and in part by the National Science Foundation, through instrumentation grant CHE 76-05582. We thank Mr. Kent Cheng for helpful discussions.

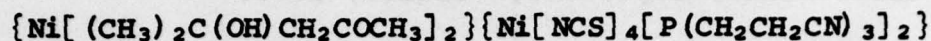
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a = 12.773, b = 12.327, c = 8.864 Å; α = 117.25, β = 101.44,
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Table I

Data for the X-Ray Diffraction Study of



(A) Crystal Data at 21(1)°C

Crystal system: triclinic ⁵	$V = 1190.3 \text{ \AA}^3$
Space group: $\bar{P}1 [C_1^1; \text{No. } 2]$	$Z = 1$
$a = 12.773(4) \text{ \AA}$	Crystal size: .16x.20x.24 mm
$b = 11.421(3) \text{ \AA}$	Formula Wt 968.5
$c = 8.864(3) \text{ \AA}$	$\rho(\text{calcd}) 1.351 \text{ g-cm}^{-3}$
$\alpha = 106.37(5)^\circ$	$\rho(\text{obsd})^a 1.34(1) \text{ g-cm}^{-3}$
$\beta = 78.56(5)^\circ$	
$\gamma = 104.37(5)^\circ$	$\mu = 35.0 \text{ cm}^{-1}(\text{CuK}\alpha)$

Cell constant determination: 12 pairs of $\pm(hkl)$ and refined $2\theta, \omega, \phi, \chi$ values in the range $50 < |2\theta| < 52^\circ$ ($\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$)

(B) Measurement of Intensity Data

Radiation: $\text{CuK}\alpha$, Ni- β -filter

Reflections measured: $-h, \pm k, \pm l$ (to $2\theta = 101^\circ$)

Scan type; speed: θ - 2θ , variable, 1.95 - $4.51^\circ/\text{min}$

Scan range: Symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]^\circ$

Background measurement: stationary, for one-quarter of scan time at each of scan limits.

No. of reflections measured: 5062 total; 4309 in unique set

Table I (cont'd)

Standard reflections: $06\bar{2}$, 024 , $\bar{2}10$, $\bar{7}20$, showed a steady decrease of 6% ($\bar{2}10$) to 15% (others) with time: An isotropic, $\sin \theta$ -dependent correction was applied⁶

Automatic recentering after every 750 reflections.

(C) Treatment of Intensity Data^b

Data reduction: intensities as before⁴; esd's of $|F_0|$ values calcd by method of finite differences, after Churchill et al.⁷

Statistical information: $R_S = 0.015 (I > 1.96\sigma(I))$; $R_{av} = 0.016$ (mainly $0kl$ reflections)

(D) Refinement,^c with 3610 data for which $F > 3.92\sigma(F)$

Weighting of reflections: $w = [\sigma^2(|F_0|) + (p|F_0|)^2]^{-1}$; $p = 0.035$

Isotropic refinement, all nonhydrogen atoms: $R = 0.116$; $R_w = 0.116$

Anisotropic refinement, all nonhydrogen atoms: $R = 0.060$; $R_w = 0.094$

Anisotropic refinement as above; isotropic refinement of hydrogen

atoms, except 3 hydrogen atoms attached to Cl6 included as fixed:

$R = 0.044$; $R_w = 0.064$

Structure factor calcn, all 4309 data: $R = 0.054$; $R_w = 0.067$

Standard deviation of an obsv'n of unit weight (SDU): 1.539

Final diffce Fourier map: $0.73 \text{ e}^-/\text{\AA}^3$ near S2; 5 other peaks $\sim 0.35 \text{ e}^-/\text{\AA}^3$ near heavy atoms; remainder: random peaks $\leq 0.29 \text{ e}^-/\text{\AA}^3$

Table I(cont'd)

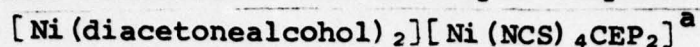
a measured by flotation in $\text{CCl}_4\text{-C}_6\text{H}_6$

b $R_s = \Sigma \sigma(|F_o|) / \Sigma |F_o|$; $R_{av} = [(\Sigma ||I| - |I_{av}|) / \Sigma |I|]$

c $R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2 / \Sigma w|F_o|^2\}^{1/2}$

SDU = $\{\Sigma w[|F_o| - |F_c|]^2 / (m-n)\}^{1/2}$ where $m(=3610)$ is the no. of obsvns and $n(=340)$ is the no. of parameters.

Table II Atomic Coordinates and Isotropic Temperature Factors for



ATOM	x	y	z	UI50
NI1	0.00000	0.00000	0.00000	
NI2	0.50000	0.00000	-0.50000	
P	-0.00885(6)	0.21850(7)	0.07827(8)	
S1	0.37149(7)	0.00480(10)	0.02770(11)	
S2	0.19697(10)	0.05694(14)	-0.50258(12)	
N1	0.16048(20)	0.03822(25)	0.04176(32)	
N2	0.05989(23)	0.01398(26)	-0.23013(32)	
N3	0.30208(31)	0.43149(37)	0.42054(52)	
N4	-0.09845(33)	0.35596(33)	-0.38034(38)	
N5	-0.21954(32)	0.46551(38)	0.08935(52)	
O1	0.52803(25)	0.11901(27)	-0.62254(35)	
O2	0.42448(25)	0.10722(27)	-0.32752(35)	
C1	0.24803(23)	0.02643(27)	0.03767(33)	
C2	0.11562(26)	0.03153(30)	-0.34307(38)	
C3	0.10901(28)	0.32387(33)	0.16614(42)	
C4	0.12313(32)	0.29610(40)	0.31974(43)	
C5	0.22496(31)	0.37133(35)	0.37719(44)	
C6	-0.00934(28)	0.29034(32)	-0.08204(39)	
C7	-0.10167(31)	0.22540(35)	-0.18184(42)	
C8	-0.10117(30)	0.29635(33)	-0.29606(39)	
C9	-0.12889(27)	0.25195(29)	0.22222(36)	
C10	-0.14321(33)	0.38785(35)	0.28506(45)	
C11	-0.18544(30)	0.43264(33)	0.17506(50)	
C12	0.51545(27)	0.23065(30)	-0.58791(42)	
C13	0.53709(42)	0.30363(47)	-0.71225(58)	
C14	0.47343(37)	0.29655(37)	-0.42709(48)	
C15	0.47528(33)	0.24334(33)	-0.28767(43)	
C16	0.40454(55)	0.30789(48)	-0.14187(57)	
C17	0.59074(47)	0.25739(56)	-0.25503(74)	
H02	0.3393(41)	0.0944(44)	-0.3678(56)	0.0898(12)
H3A	0.1637(38)	0.3873(40)	0.0780(53)	0.0713(10)
H3B	0.0947(32)	0.4053(38)	0.1749(45)	0.0580(8)
H4A	0.1255(41)	0.2158(48)	0.3080(57)	0.0821(12)
H4B	0.0639(51)	0.3190(55)	0.4024(71)	0.1169(16)
H6A	0.0480(37)	0.2853(38)	-0.1451(50)	0.0637(10)
H6B	-0.0046(26)	0.3756(32)	-0.0460(36)	0.0360(6)
H7A	-0.1706(36)	0.2220(36)	-0.1147(47)	0.0602(9)
H7B	-0.0917(32)	0.1559(39)	-0.2250(47)	0.0535(9)
H9A	-0.1966(30)	0.2014(32)	0.1715(41)	0.0466(7)
H9B	-0.1211(31)	0.2189(34)	0.3155(45)	0.0531(8)
H10A	-0.0725(37)	0.4469(40)	0.3077(51)	0.0698(10)
H10B	-0.1884(39)	0.4033(42)	0.4050(57)	0.0836(11)
H13A	0.5870(45)	0.3918(51)	-0.6730(60)	0.0932(12)
H13B	0.4616(60)	0.3172(62)	-0.7292(79)	0.1378(18)
H13C	0.5687(42)	0.2610(46)	-0.7923(61)	0.0808(12)
H14A	0.5038(46)	0.3891(55)	-0.4041(64)	0.1075(14)
H14B	0.4063(40)	0.3009(41)	-0.4202(53)	0.0701(10)
H16A	0.4334	0.3950	-0.1172	0.1773
H16B	0.4049	0.2750	-0.0530	0.1773
H16C	0.3320	0.2925	-0.1639	0.1773
H17A	0.6158(44)	0.3584(51)	-0.2275(61)	0.0915(12)
H17B	0.6462(52)	0.2348(56)	-0.3390(75)	0.1163(18)
H17C	0.5879(43)	0.2184(51)	-0.1608(63)	0.0979(13)

^a Standard deviations in the least significant digit appear in parentheses

in this and subsequent tables

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Table III Anisotropic Temperature Factors (\AA^2) for $[\text{Ni}(\text{diacetonealcohol})_2][\text{Ni}(\text{NCS})_4\text{CEP}_2]$ ^a

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N11	0.02908(34)	0.03799(37)	0.03246(35)	0.01121(26)	-0.00403(25)	0.00720(26)
N12	0.04812(43)	0.04325(41)	0.04161(40)	0.01299(32)	-0.00200(31)	0.01410(31)
P	0.03658(37)	0.03649(38)	0.03467(37)	0.01061(28)	-0.00758(28)	0.00710(28)
S1	0.0349(4)	0.0964(7)	0.0576(5)	0.0236(4)	-0.0043(3)	0.0263(5)
S2	0.0676(7)	0.1324(11)	0.0481(5)	-0.0119(7)	-0.0051(5)	0.0379(6)
N1	0.0351(14)	0.0478(15)	0.0497(15)	0.0124(11)	-0.0077(11)	0.0070(11)
N2	0.0520(16)	0.0530(16)	0.0456(15)	0.0190(13)	-0.0020(13)	0.0145(12)
N3	0.0658(22)	0.0783(24)	0.1004(30)	0.0181(19)	-0.0437(22)	-0.0058(21)
N4	0.0939(26)	0.0742(21)	0.0510(18)	0.0247(19)	-0.0131(17)	0.0273(16)
N5	0.0741(24)	0.0854(26)	0.1000(29)	0.0273(20)	-0.0028(21)	0.0512(23)
O1	0.0784(19)	0.0679(17)	0.0692(17)	0.0201(14)	-0.0016(14)	0.0264(14)
O2	0.0710(18)	0.0675(17)	0.0678(17)	0.0218(14)	0.0006(14)	0.0206(13)
C1	0.0360(15)	0.0425(15)	0.0343(14)	0.0081(12)	-0.0072(11)	0.0086(12)
C2	0.0436(16)	0.0498(17)	0.0412(17)	0.0107(13)	-0.0104(14)	0.0115(13)
C3	0.0441(17)	0.0474(18)	0.0498(19)	0.0087(14)	-0.0125(15)	0.0086(14)
C4	0.0518(20)	0.0629(23)	0.0440(19)	0.0111(17)	-0.0151(15)	0.0033(16)
C5	0.0575(21)	0.0610(22)	0.0546(20)	0.0238(18)	-0.0219(17)	-0.0054(17)
C6	0.0434(17)	0.0454(18)	0.0416(16)	0.0115(14)	-0.0051(13)	0.0152(14)
C7	0.0560(20)	0.0471(19)	0.0425(17)	0.0111(15)	-0.0126(15)	0.0142(15)
C8	0.0559(19)	0.0560(19)	0.0418(17)	0.0154(15)	-0.0093(14)	0.0125(15)
C9	0.0471(17)	0.0434(16)	0.0377(15)	0.0169(13)	-0.0047(13)	0.0062(13)
C10	0.0589(21)	0.0523(20)	0.0533(20)	0.0262(17)	-0.0098(16)	0.0009(15)
C11	0.0518(20)	0.0483(19)	0.0743(24)	0.0178(16)	0.0022(17)	0.0204(17)
C12	0.0436(16)	0.0426(17)	0.0566(19)	0.0091(13)	-0.0062(14)	0.0106(14)
C13	0.0755(28)	0.0695(27)	0.0648(26)	0.0248(23)	0.0049(22)	0.0351(22)
C14	0.0612(23)	0.0530(22)	0.0618(22)	0.0179(18)	-0.0096(18)	0.0172(17)
C15	0.0711(23)	0.0486(18)	0.0470(18)	0.0203(17)	-0.0090(16)	0.0076(15)
C16	0.1463(50)	0.0756(30)	0.0610(26)	0.0547(32)	0.0110(29)	0.0125(22)
C17	0.0791(33)	0.0893(36)	0.0831(34)	0.0090(27)	-0.0357(28)	0.0198(28)

^a The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \dots + 2b^*c^*U_{23}kl)]$

Table IV

Selected Bond Lengths (Å) and Angles (deg)

(A) $[\text{Ni}(\text{diacetonealcohol})_2]^{2+}$

Ni2-O1	1.895 (3)	C15-C16	1.536 (7)
Ni2-O2	1.927 (3)	C15-C17	1.520 (8)
O1-C12	1.268 (5)	C15-O2	1.498 (5)
C12-C13	1.506 (6)	O2-HO2	1.174 (54)
C12-C14	1.476 (5)	C-H(methyl)	0.996 (25) ^a
C14-C15	1.529 (6)	C-H(methylene)	0.924 (41) ^a
O1-Ni2-O2	90.30 (13)	C14-C15-C17	112.06 (38)
Ni2-O1-C12	132.14 (27)	C14-C15-C16	108.26 (36)
O1-C12-C13	121.64 (35)	C14-C15-O2	108.43 (32)
O1-C12-C14	123.32 (34)	C16-C15-C17	111.78 (41)
C13-C12-C14	114.96 (35)	Ni2-O2-C15	117.45 (24)
C12-C14-C15	118.10 (35)	C15-O2-HO2	108.8 (25)
C17-C15-O2	108.21 (36)	Ni2-O2-HO2	104.0 (25)
C16-C15-O2	107.96 (35)		

B. $[\text{Ni}(\text{NCS})_4\text{CEP}_2]^{2-}$

Ni1-N1	2.072 (3)	C5-N3	1.120 (6)
Ni1-N2	2.068 (3)	P-C6	1.832 (4)
Ni1-P	2.420 (1)	C6-C7	1.527 (5)
N1-C1	1.152 (4)	C7-C8	1.463 (5)
C1-S1	1.637 (3)	C8-N4	1.135 (5)
N2-C2	1.144 (4)	P-C9	1.834 (3)
C2-S2	1.632 (3)	C9-C10	1.538 (5)
P-C3	1.833 (4)	C10-C11	1.460 (6)
C3-C4	1.535 (5)	C11-N5	1.132 (6)
C4-C5	1.467 (6)	C-H(methylene)	0.956 (13) ^a

Table IV (cont'd)

N11-N1-C1	160.77 (26)	N1-C1-S1	177.99 (29)
N11-N2-C2	163.90 (28)	N2-C2-S2	179.00 (33)
N1-N11-N2	87.60 (11)	C4-C5-N3	178.18 (45)
N1-N11-P	92.46 (8)	C7-C8-N4	176.96 (41)
N2-N11-P	90.21 (8)	C10-C11-N5	178.80 (45)

^a Weighted average

Table V

Least-Squares Planes for $[\text{Ni}(\text{diacetonealcohol})_2][\text{Ni}(\text{NCS})_4\text{CEP}_2]^a$

Plane No. 1, Equation: $-0.9374X - 0.2819Y - 0.2047Z + 4.6232 = 0$

Atoms in Plane: Ni2, O1, C12, C13, C14

Distances: Ni2 0.023 C13 0.027 (6) C15 -0.382 (4)
 O1 -0.028 (3) C14 0.002 (5) O2 0.400 (3)
 C12 -0.025 (4)

Plane No. 2, Equation: $0.2042X - 0.9386Y - 0.2783Z = 0$

Atoms in Plane: Ni1, N1, N2

Distances: C2 -0.049 (3) S2 -0.117 (2)

Plane No. 3, Equation: $0.1142X + 0.3069Y - 0.9449Z = 0$

Atoms in Plane: Ni1, N1, P

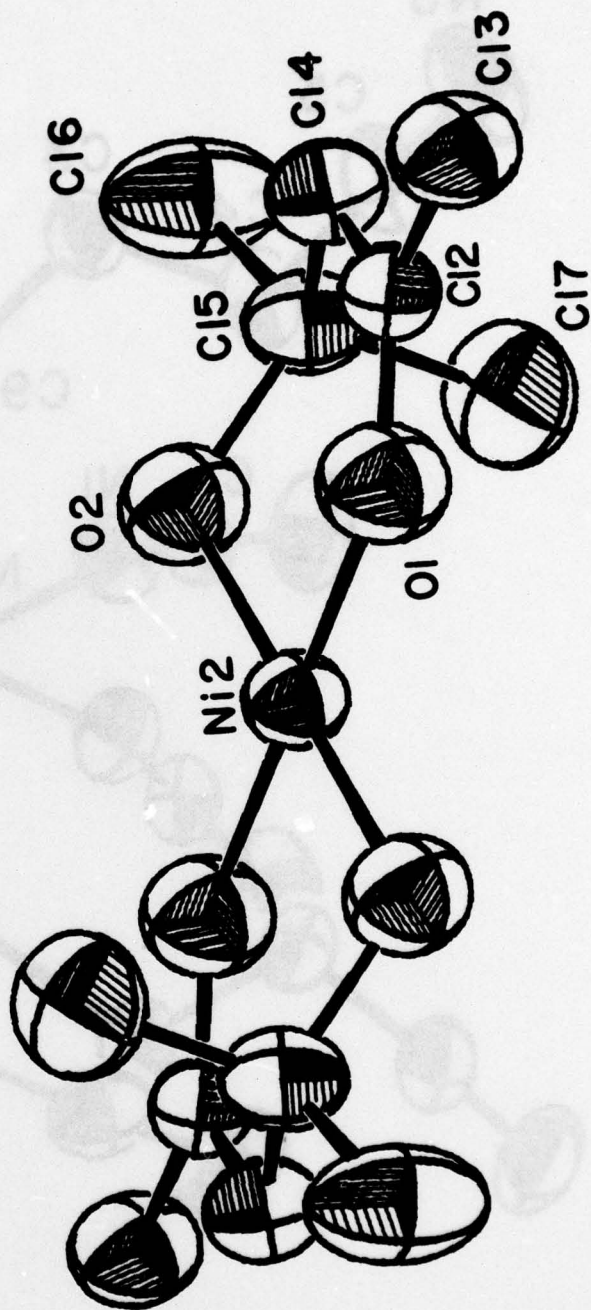
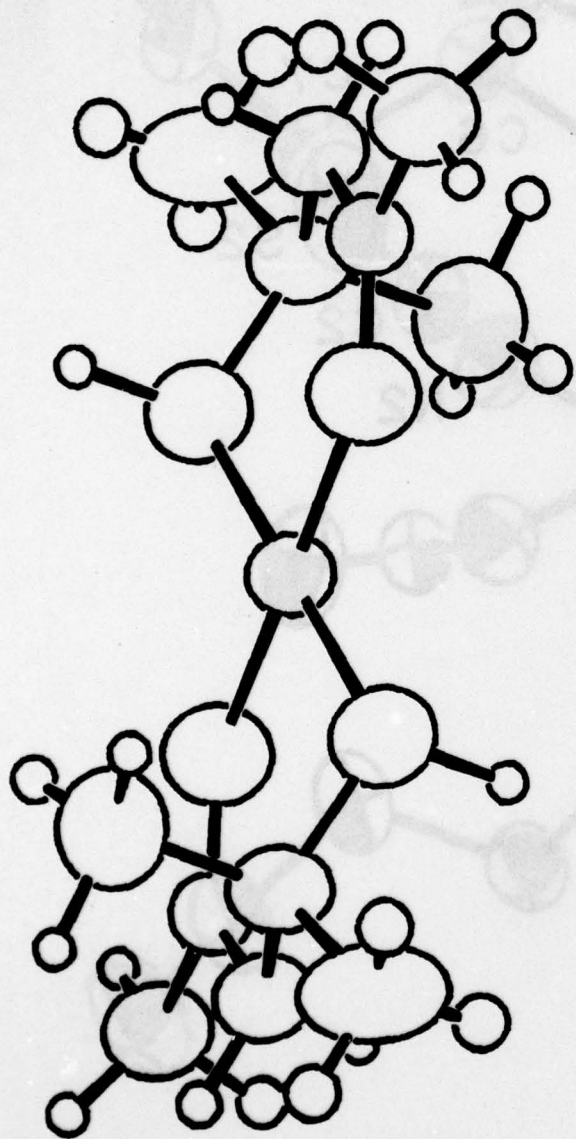
Distances: C1 0.126 (3) S1 0.323 (1)

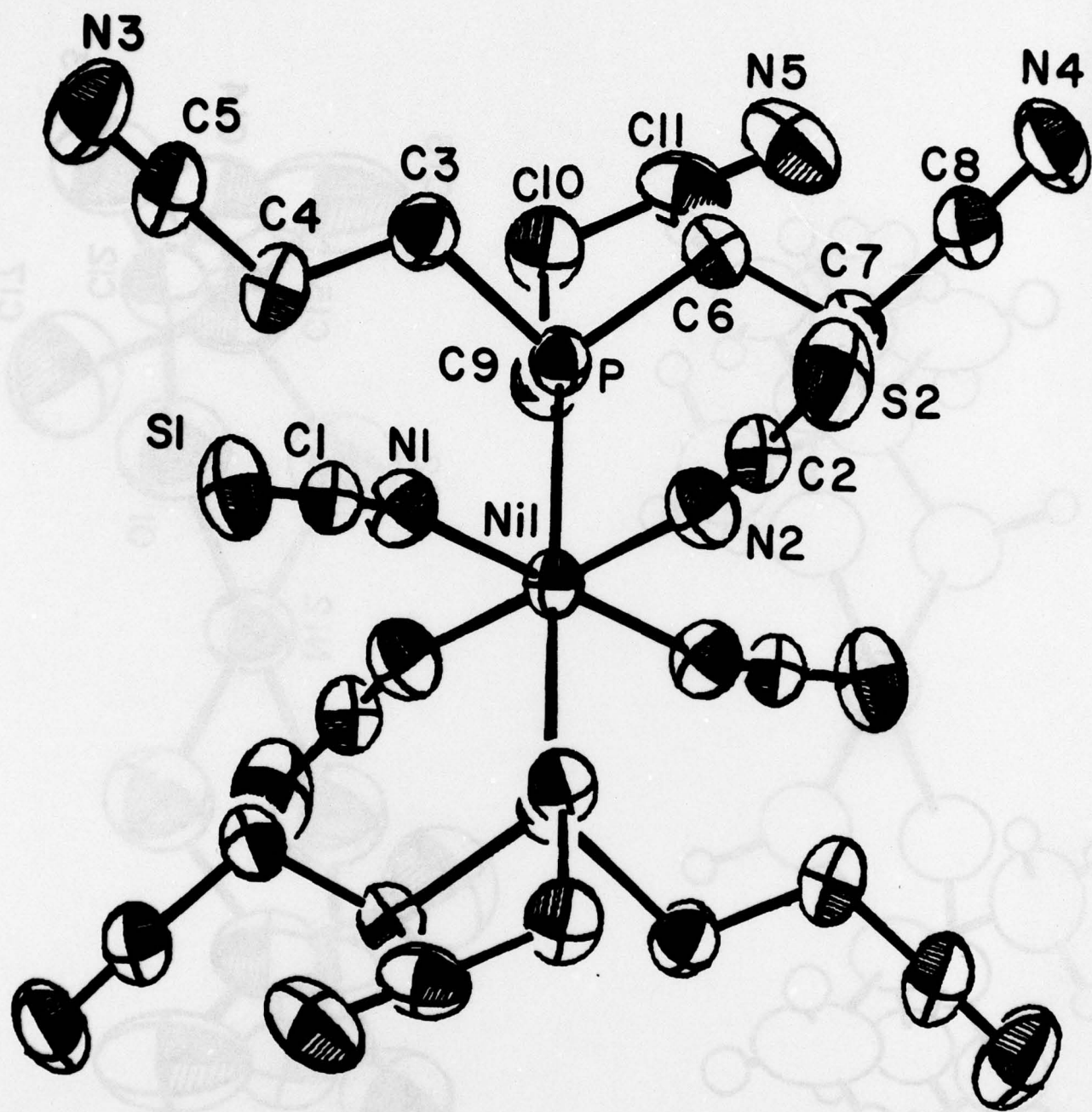
^a Orthogonal coordinates X, Y, Z used in these calculations were obtained from fractional coordinates using the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b \cos \gamma & c \cos \beta \\ 0 & b \sin \gamma & -c \sin \beta \cos \alpha^* \\ 0 & 0 & 1/c^* \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Figure Legends

1. Molecular structure of the $\{\text{Ni}[(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3]_2\}^{2+}$ ion, showing (A) location of all atoms, including hydrogen, and (B) 50% probability ellipsoids for atoms refined anisotropically.
2. Molecular structure of the $\{\text{Ni}[\text{NCS}]_4[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2\}^{2-}$ ion.
3. A stereoscopic view of the unit cell contents.





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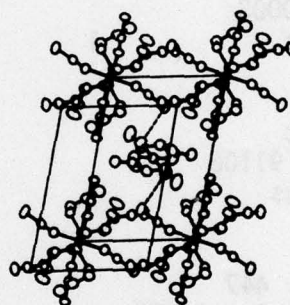
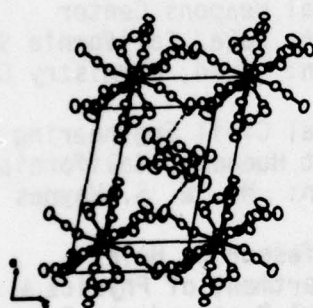
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Fig. 3



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